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C. E. Knight Applied Engineering Company P. O. Box 1327 Orangeburg, S. C. 29115 (803) 534-2424	

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FINAL RESEARCH REPORT
E–19–657

ANALYSIS OF NiCr SURFACE CLADDING AND ITS RESISTANCE TO SULFIDIZATION

By
Robin D. Taylor
Robert F. Hochman

Prepared for:
APPLIED ENGINEERING COMPANY
ORANGEBURG, S.C. 29115

MAY 1, 1978

GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING
ATLANTA, GEORGIA 30332

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Robin D. Taylor and Robert F. Hochman
Metallurgy Department, School of Chemical Engineering

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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I. INTRODUCTION

Corrosion of metals and alloys by hydrogen sulfide and sulfur bearing radicals in aqueous and gaseous environments has been a significant problem in industry for many decades. Extensive research and data compilation has been performed to evaluate the resistance to such attack of a wide range of metals and alloys.[1,2,3,4...]

Hydrogen sulfide directly attacks the surface of some of the commonly used structural metals, reacting rapidly at lower temperatures to form metal sulfides and decreasing the effective wall thickness of the equipment.

The presence of chromium in alloy steels has been repeatedly shown to greatly increase the resistance to sulfide corrosion.[1,2] This has been attributed to the formation of an inner scale at the interface, primarily an iron-chromium spinel ($FeCr_2S_4$). Most alloys with 12% or more chromium require exposures up to 400 hours at 500°C to form an equilibrium spinel scale.[2]

Nickel is not particularly resistant to sulfide attack, and if present in very high concentrations, may be detrimental to the protective action offered by chromium.[1,3]

The studies reported will attempt to evaluate the effectiveness of a nickel-chromium protective coating in improving the sulfide corrosion resistance of plain carbon heat exchanger finned tubes for a temperature range to 500°F. The economics of using a relatively inexpensive base metal with a protective coating are attractive compared to the alternatives of fabricating the entire piece of equipment out of relatively expensive alloys or the replacement of corroded mild steel.

II. OBJECTIVES

The purpose of these studies is to compare the corrosion resistance of the plain carbon steel and the nickel-chromium surface-treated steel in specified

environments, particularly hydrogen sulfide.

The studies consist of three phases:

A. Electrochemical polarization analysis to initially determine differences in the surface electrochemical characteristics of the two materials.

B. Chemical and metallurgical analysis to establish the compositional and microstructural differences between the surface-treated and plain carbon steels.

C. Elevated temperatures analysis of the sulfidization attack on the surface of coated material vs. plain carbon material for programmed periods of exposure.

The methods and environments employed, while precisely representative of conditions met in industrial practice, provide simple and more easily obtainable parameters for a general comparative evaluation.

III. EXPERIMENTAL RESULTS

A. Electrochemical Polarization Analysis

Anodic polarization curves of the plain carbon steel and the surface-treated material were obtained in dilute sulfuric acid solutions.

The standard corrosion cell used for this test consisted of a closed cylindrical glass vessel with diametrically introduced working electrode and platinum counter electrode. A Luggin probe, in electrolytic contact with the reference saturated calomel electrode (SCE) by means of a salt bridge, was situated within 2 mm of the working electrode surface. Nitrogen was bubbled through the electrolyte solution for deoxygenation

A standard sweep rate of 0.6 V/hr., (10 steps/min and 1 mV/step) was used for all polarization studies.

The anodic polarization curves of both materials in 0.1 N H_2SO_4 (4700 ppm SO_4, pH 1.4) are shown in Figure 1. The vertical axis is the impressed voltage of

the anode relative to the SCE (+ 0.242 V - SHE), and the horizontal axis is the resultant current density, recorded as Amps/cm^2. A prominent feature of these curves for the plain carbon steel and the surface-treated material is the comparatively higher nobility of the treated material as evidenced by the more positive rest potential. Also, the slopes of the curves provide a significant indication of the materials' relative resistance to attack.

The sigmoidal shape of the curve for the surface-treated material indicates that as the voltage is increased the current density initially increases slowly, then at higher voltages the current density rises substantially. The Tafel constant (voltage increase/decade current density increase) goes from a low value to a higher value then back to a lower value as the anodic polarization curve is tranversed. This would indicate a tendency toward passivation (or what could be described as pseudo passivation). The curve in Figure 1 for the surface treated material is not true passivation in the classical sence of the phenomena where a negative Tafel constant and substantial current decrease in the passive region are obvious. Alternatively, the plain carbon material exhibits a nearly constant Tafel slope, much lower than that of the surface-treated material in the same region.

Figure 2 shows the anodic polarization curves of both materials in 0.01 N H_2SO_4 (470 ppm SO_4, pH 2.2). The curves and relationships are similar to those of Figure 1. The most evident difference is the extension of the higher Tafel constant over the entire voltage range studied for the surface treated material.

These studies demonstrate an electrochemical superiority of the surface treated material over the plain carbon material with regard to resistance to attack in sulfate bearing aqueous solutions.

B. Chemical and Metallurgical Analysis

The microstructures of the plain carbon material and the surface treated material were first examined by optical microscopy to determine any visible differences.

Figure 3 shows a cross-section of the surface treated material. The base material is plain carbon steel consisting of small equiaxed ferrite grains with widely dispersed coarse pearlite colonies. The pearlite appears to be less abundant near the surface of the base metal indicating some surface decarburization during fabrication. At higher magnification the surface coating is quite evident. While the outer surface of the coating is relatively smooth, the surface contours of the base metal result in an irregular coating with a thickness averaging about eight microns.

Figure 4 shows the surface topagraphy of the protective coating. The large elongated grains evident are indicative of the extended heating during the "diffusion cladding" process to form the protective coating.

Figure 5 shows a cross section of the regular plain carbon material for comparison. The ferrite grains are smaller, and the less pearlite indicates a low carbon content.

The microstructures and chemistry of the two base steels are similar enough that any significant differences in sulfidization resistance must be attributed to differences due to the surface cladding vs. the non clad or coated surface.

A microprobe analysis of the surface treated material was performed to confirm the presence of and distribution of the nickel and chromium constituents of the surface coating. The technique is essentially an elementally selective scan- and -identify analysis A polished cross-section of the surface-treated material was used for the analysis, the results are shown in Figure 6. As expected,

high nickel and chromium concentrations were found in the surface coating. These results were supported by scanning electron microscopy--x-ray analysis of the metal.

C. Elevated Temperature Studies.

Samples of the surface treated material and plain carbon steel were exposed to an elevated temperature sulfidizing-oxidizing environments to compare their resistance to corrosive attack. A gas mixture of 10 wt% H_2S in air saturated with water vapor at 20°C was used for all experiments.

The temperature dependence studies consisted of a 20 hr. exposure time at atmospheric pressure and a gas flow rate of 25 cc/min. Relative attack of the plain and surface treated materials was determined by weight gain measurements. The weight gain is a result of the build up of corrosion products. For exposures of short duration, weight gain data provides a straight forward and reliable parameter for comparison of reactivity, since the degree of corrosion is evidenced by the formation of sulfides, sulfates, and oxides. The results of the temperature dependence studies are shown graphically in Figures 7 & 8 as % weight gain vs. temperature and weight gain per unit area vs. temperature, respectively, (sample size was equal in each case).

A preliminary time dependence study was also performed. The same gas mixture was used as for the temperature dependence study. The samples were exposed at 500°C for 20, 40, and 80 hours. The results of this study are shown graphically in Figure 9 as % weight gain vs. time.

Comparison of the data clearly indicates the superior corrosion resistance of the nickel-chromium surface treated materials over the plain carbon material.

The results of the wright gain comparisons are supported by microscopic examination. Figure 10 shows a cross section of the plain carbon material after exposure at 500°C for 80 hours. Figure 11 shows a cross section of the surface

treated material exposed under the same conditions. A thick scale is evident on the plain carbon steel, whereas there is little or no apparent deterioration of the surface coating of the treated material. The only noticeable change is the formation of a small amount of precipitate on the surface of the coating and at interface of the base steel and surface coating. The interface precipitate has been studied by electron microprobe analysis and found to have Fe, Cr, and Ni plus sulfur, which is high in some localized areas. Figures 12a, b, c and d provide a pictoral characterization of the microprobe analysis for FeCr, Ni and S and Figure 13 shows scans across the interface for these elements. The importance and stability, or instability, of this intermediate layer can only be determined after long term exposure to sulfur bearing gases. Such tests were not part of the original program because the accelerated studies were designed to develop the basic corrosion data. However, if this intermediate layer becomes a stable Fe, Cr, Ni, S phase precluding further attack, or if the S penetration to the coating--base metal interface results in continuous growth of the interface precipitate with deterioration and disruption of the surface coating is now a major question with regard to the effectiveness of the coating.

IV. Conclusions:

The preliminary investigations have indicated a marked improvement in resistance to sulfidization attack as a result of the application of the nickel-chrome diffusion clad layer. The stability or instability of the high sulfur interface precipitate must be determined in longer term tests. The usefulness of the coating will be dependent on this long term stability.

The polarization tests demonstrated improved electrochemical properties for the clad steel in dilute sulfuric acid solutions in the form of increased nobility and lower cut-off current density.

Metallography and micro probe analysis established the existence and integrity of a discrete protective layer on the surface. However, these studies also established the penetration of sulfur through the coating to produce an interface (coating--base metal) precipitate whose stability and protective capabilities are in question until much longer term accelerated studies can be performed.

Exposure in our high temperature reactor and subsequent analysis have provided evidence of the improved corrosion resistance of the surface treated material in simulated industrial gas environments.

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3. McKay, Robert J. and Worthington, Robert, Corrosion Resistance of Metals and Alloys, Reinhold Publishing Corp., New York, 1936.

4. LaQue, F. L., and Copson, H. R., Corrosion Resistance of Metals and Alloys Reinhold Publishing Corp., New York, 1963.

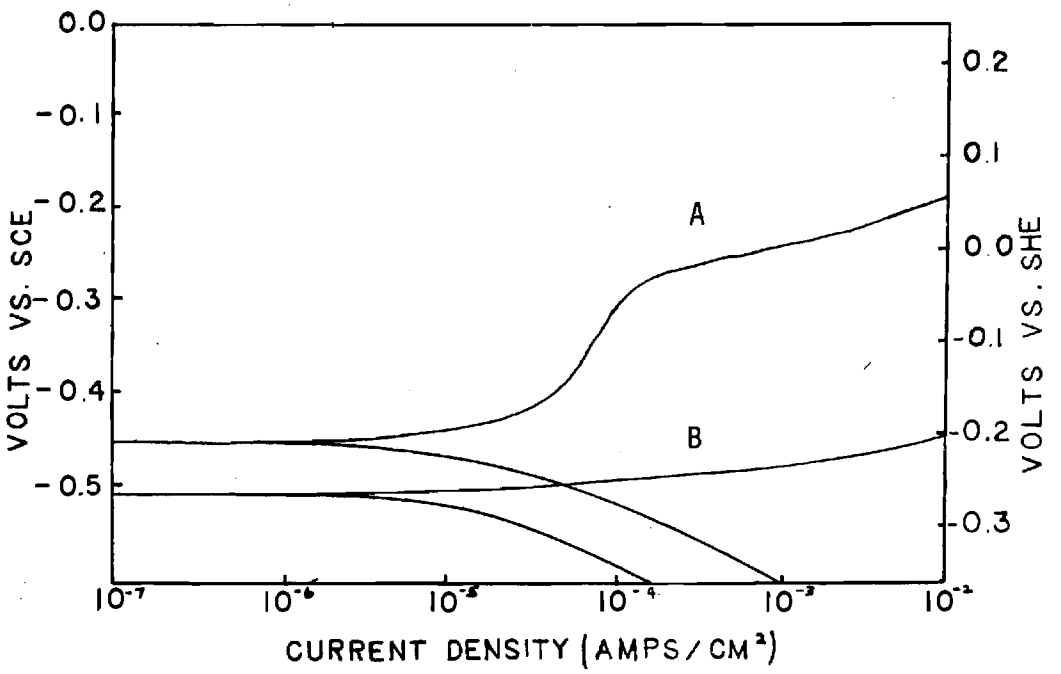


Figure 1. Anodic polarization curves in 0.1 N H_2SO_4
A. Ni-Cr Diffusion-Clad Steel
B. Mild Steel

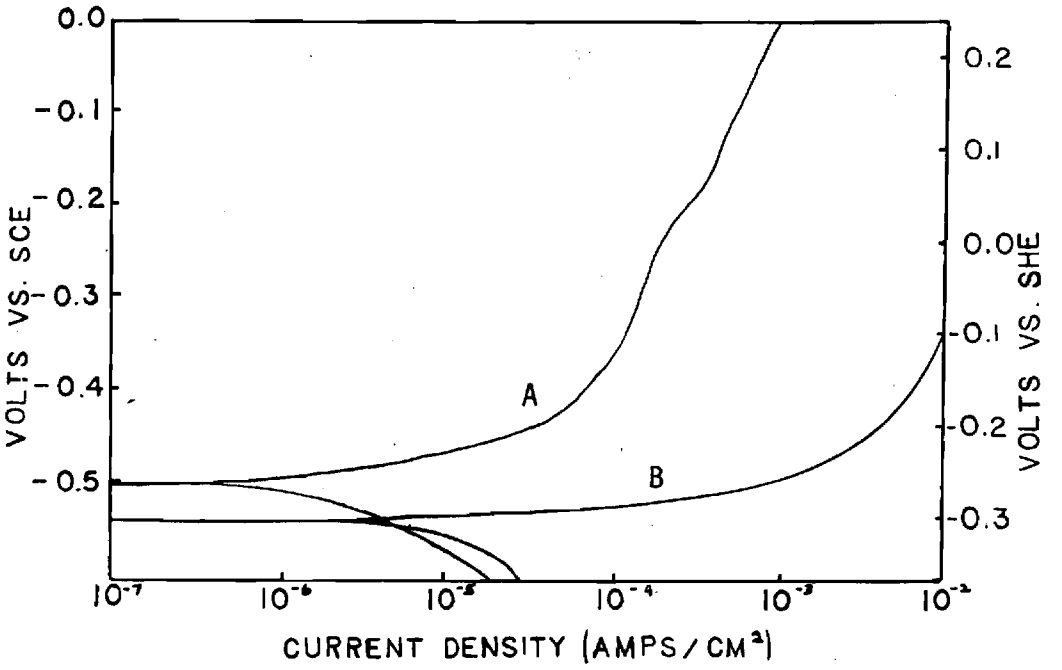
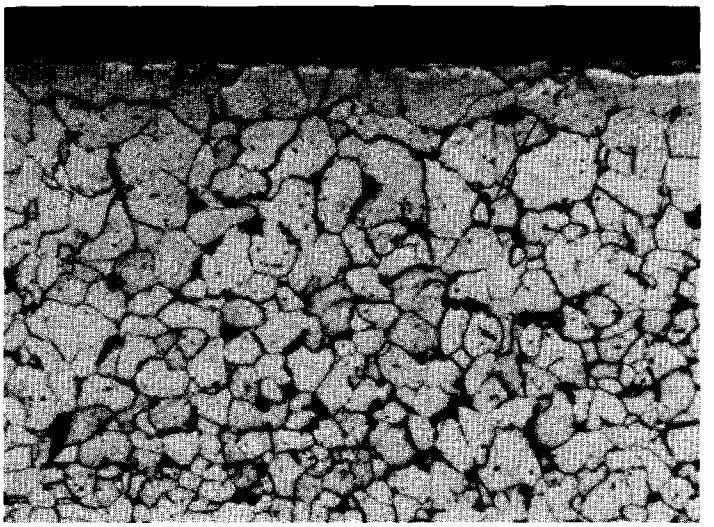
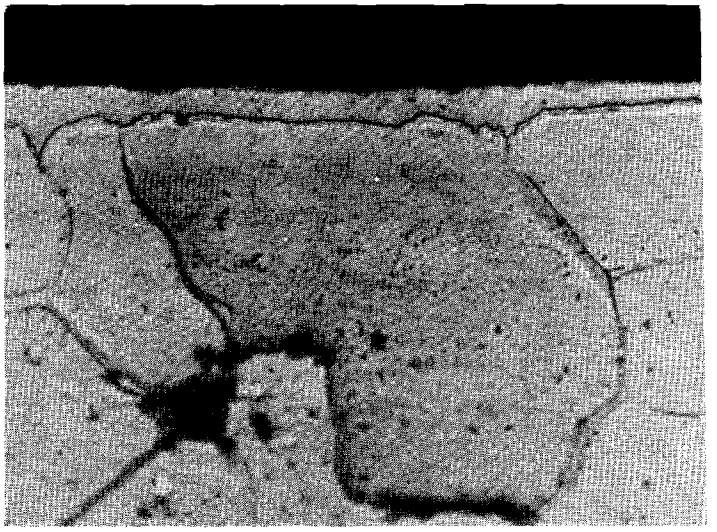


Figure 2. Anodic polarization curves in 0.01 N H_2SO_4
A. Ni-Cr Diffusion Clad Steel
B. Mild Steel



A

100X



B

500X

Figure 3. Nickel-Chromium Diffusion Clad Steel.
A. 100X
B. 500X

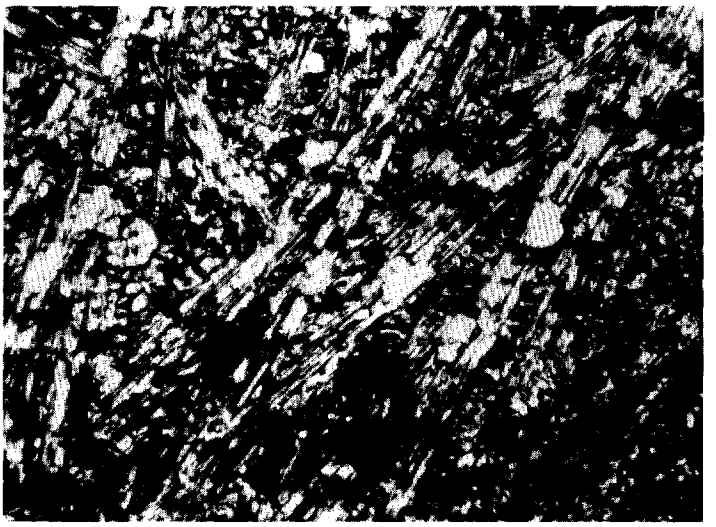


Figure 4. Nickel-Chromium Diffusion Cladding Surface. 100X

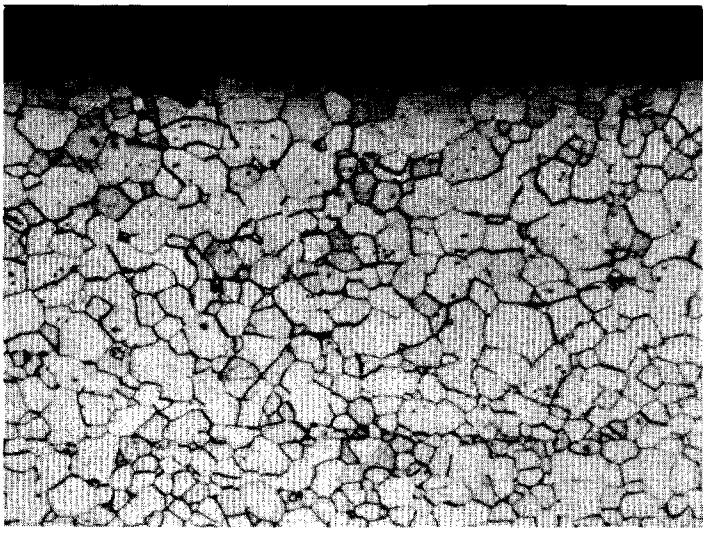


Figure 5. Mild Steel. 100X

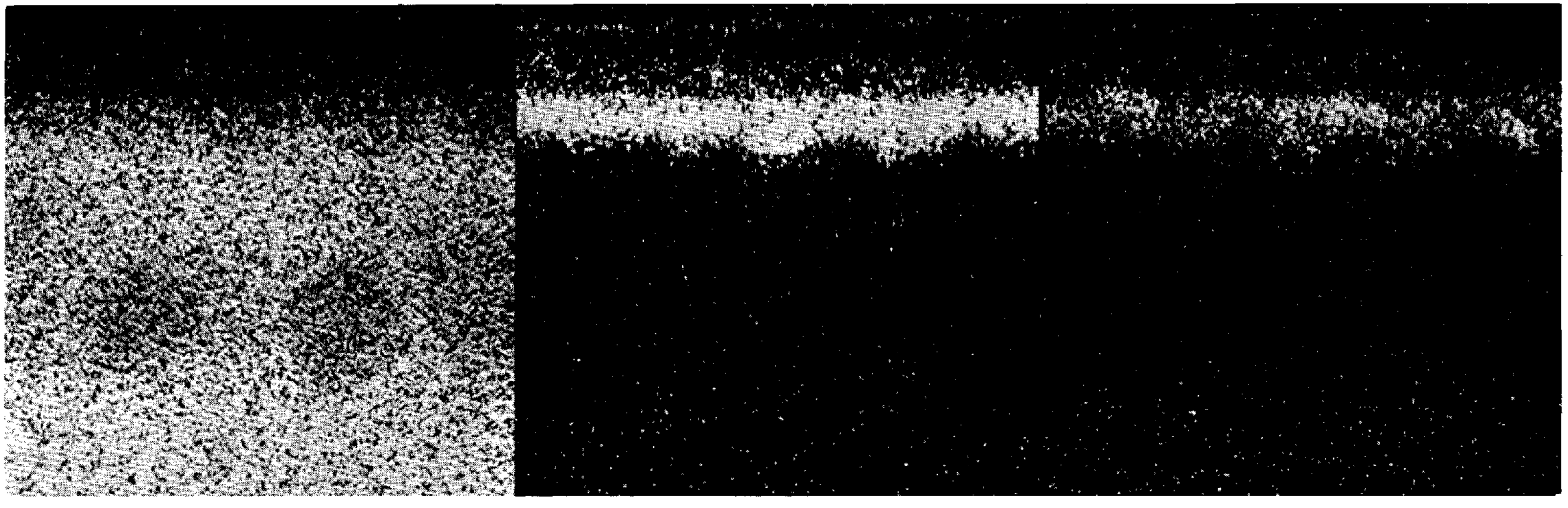


Figure 6. Microprobe Analysis 500X. Elemental Profile

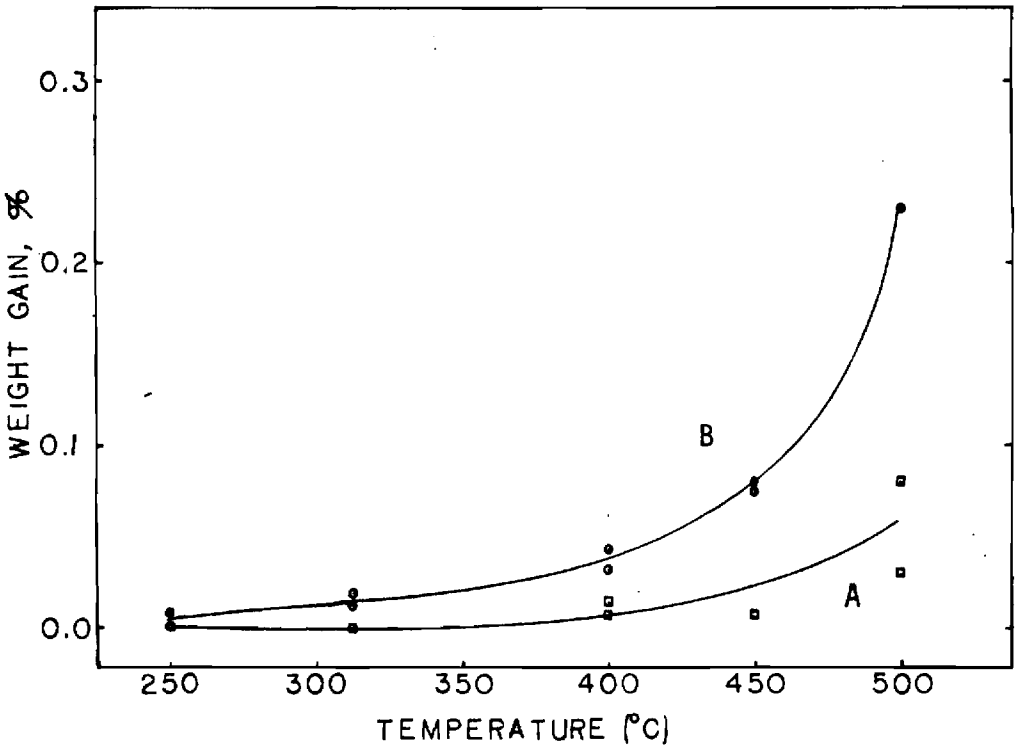


Figure 7. Reactivity vs. Temperature 10 wt% H_2S in Air, 20 hrs.
A. Ni-Cr Diffusion Clad Steel
B. Mild Steel

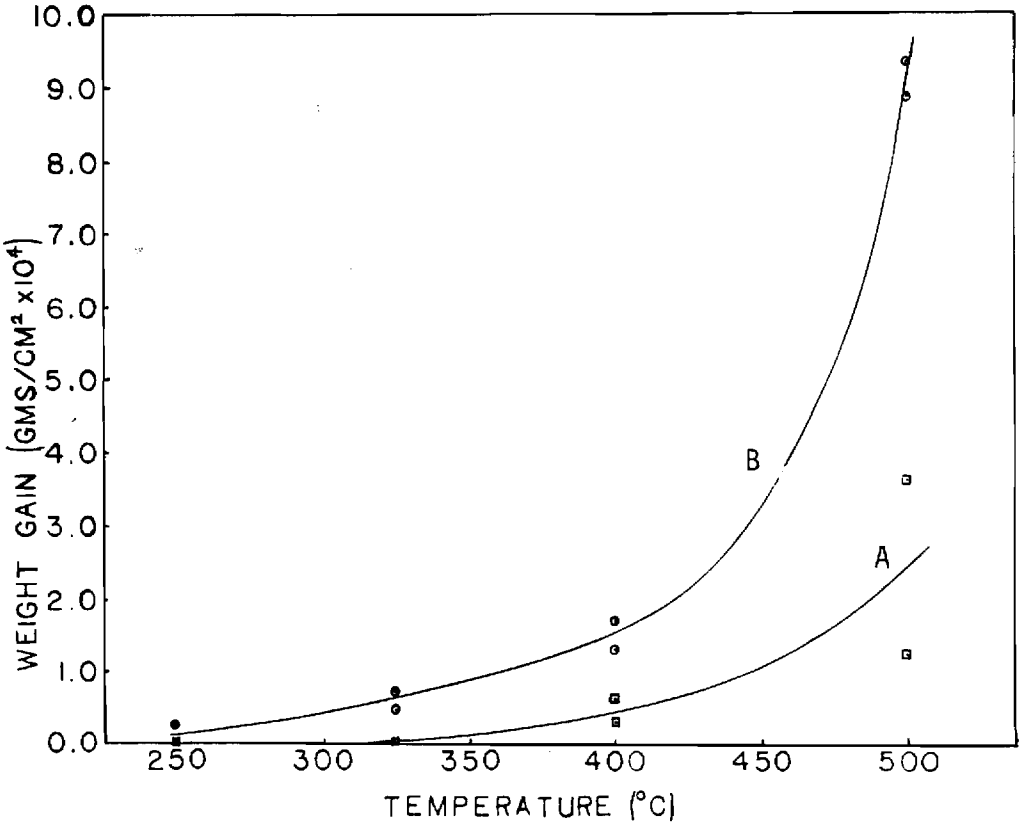


Figure 8. Reactivity vs. Temperature 10 wt% H_2S in Air, 500°C
A. Ni-Cr Diffusion Clad Steel
B. Mild Steel

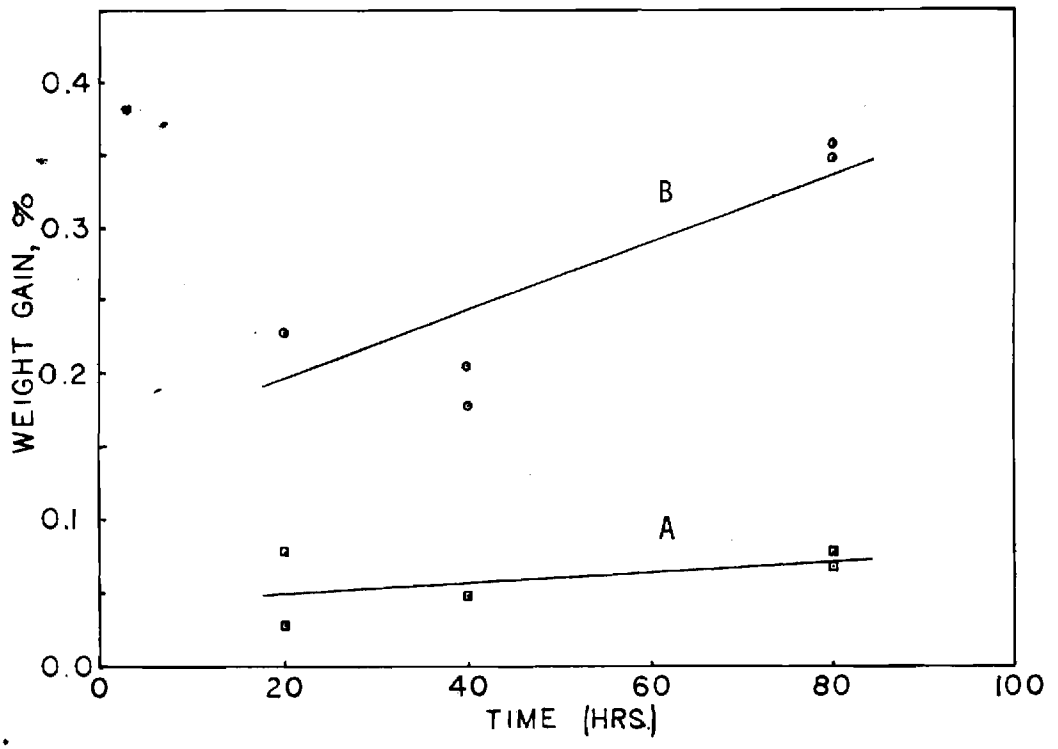


Figure 9. Reactivity vs. Time 10 wt% H_2S Air, 500°C
A. Ni-Cr Diffusion Clad Steel
B. Mild Steel

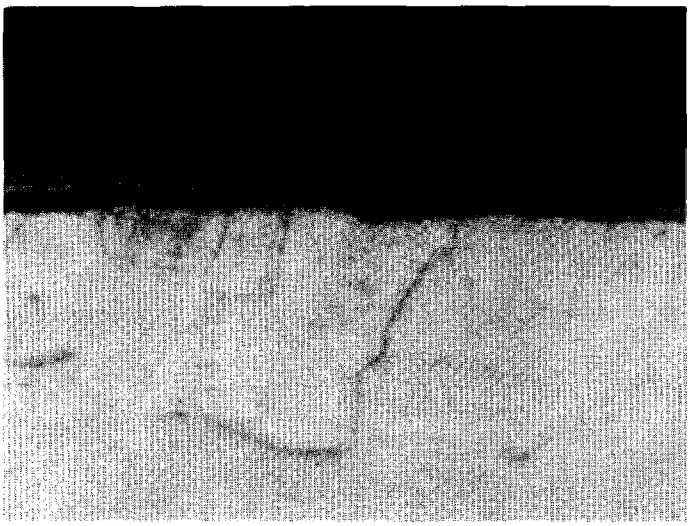


Figure 10. Mild Steel 80 hr. exposure 10 wt% H_2S in Air, 500°C 500X.

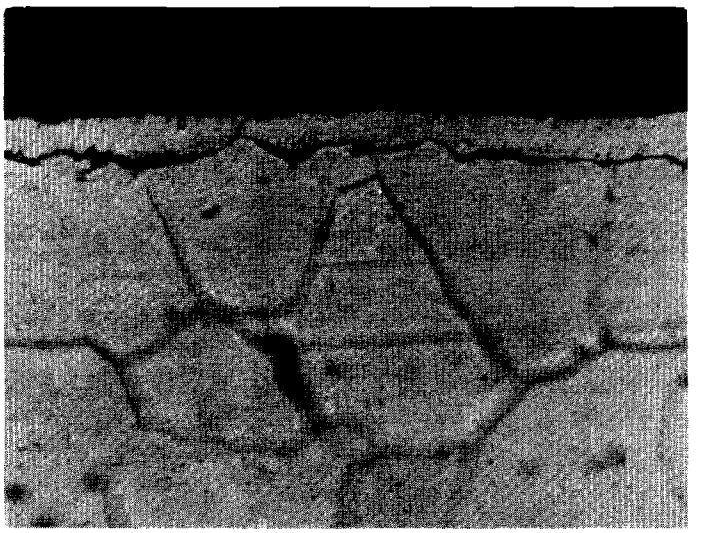


Figure 11. Ni-Cu Diffusion Clad Steel 80 hr. exposure 10 wt% H_2S in Air, 500°C. 500X

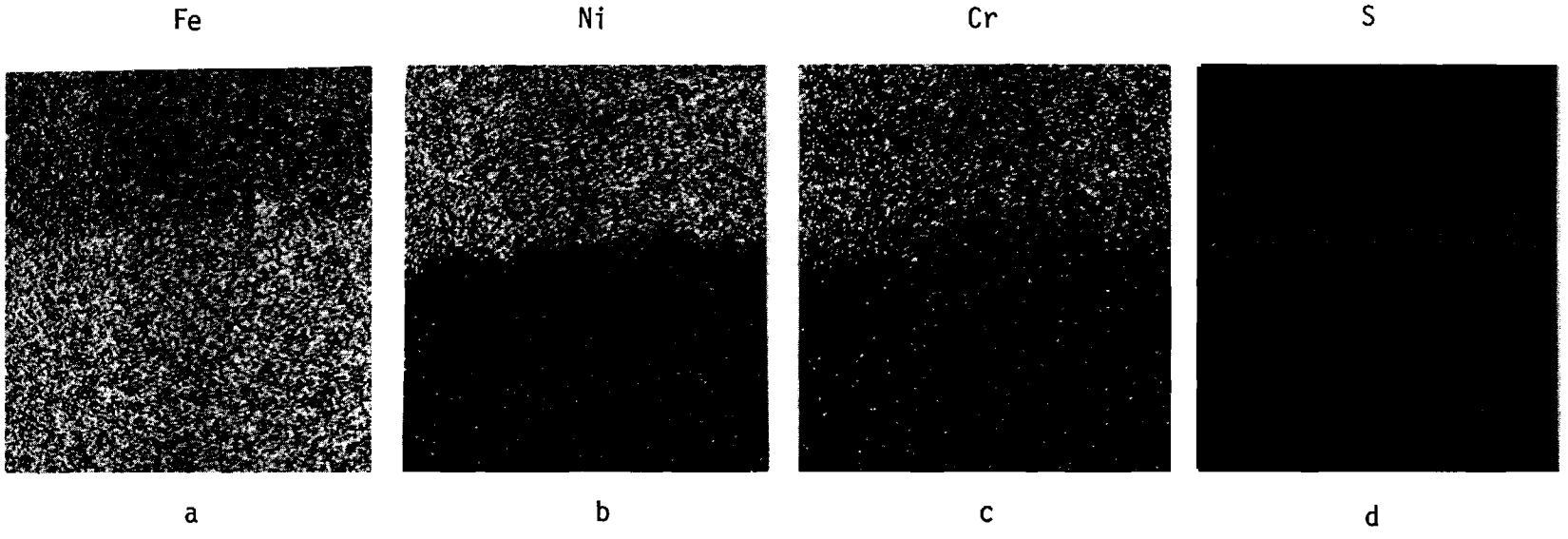


Figure 12. Elemental Microprobe Analysis Across the Steel-NiCr Interface After Reaction. X400

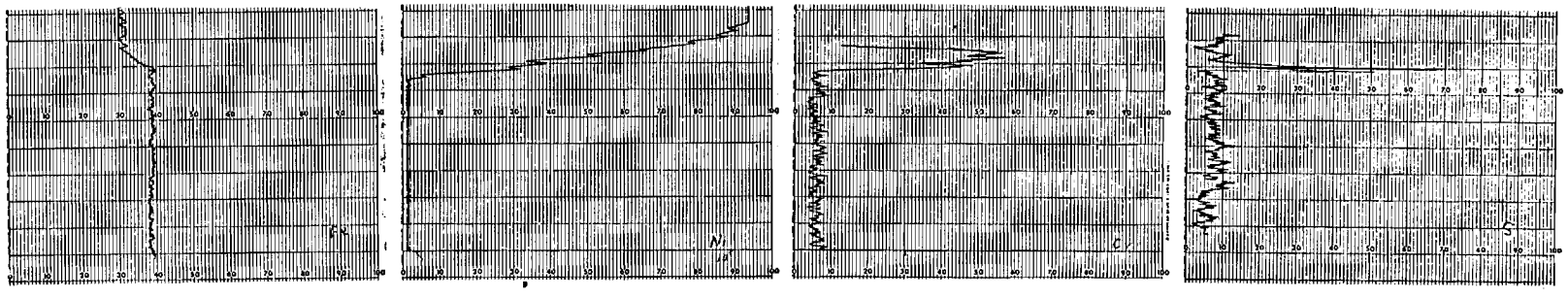


Figure 13. Microprobe Scans Across the Steel-NiCr Interface After Reaction.